

Ring-Opening Polymerization of Trimethylenecarbonate and Its Copolymerization with ϵ -Caprolactone by Lanthanide (II) Aryloxy Complexes

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ABSTRACT: Lanthanide metal (II) 2,6-di-*tert*-butylphenoxy complexes (ArO)₂Ln(THF)₃ (Ln = Sm **1**, Yb **2**) alone have been developed to catalyze the ring-opening polymerization of trimethylenecarbonate (TMC) and random copolymerization of TMC and ϵ -caprolactone (ϵ -CL) for the first time. The influence of reaction conditions, such as initiator, initiator concentration, polymerization temperature, and polymerization time, on monomer conversion, molecular weight, and molecular weight distribution of the resulting PTMC was investigated. It was found that the

divalent complex **1** showed higher activity for the polymerization of TMC than complex **2**. The random structure and thermal behavior of the copolymers P(TMC-*co*-CL) have been characterized by ¹H NMR, ¹³C NMR, GPC, and DSC analysis. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1383–1389, 2007

Key words: lanthanide (II) aryloxy complex; trimethylenecarbonate; ϵ -caprolactone; ring-opening polymerization; copolymerization

INTRODUCTION

The preparation of homopolymers of aliphatic cyclic carbonates and copolymers of cyclocarbonates and lactones has attracted considerable attention for their mechanical and biological properties which are useful in various areas, such as agriculture and biomedicine.^{1–6} Many kinds of cyclic carbonates, such as 1,3-trimethylenecarbonate (TMC), 2,2-dimethyltrimethylene carbonate (DTC), 1-methyltrimethylene carbonate (MTC) etc., have been found to polymerize by cationic, anionic, coordination-insertion, or enzymatic ring-opening polymerization mechanisms.^{6–13} The ring-opening polymerization via a coordination-insertion mechanism is carried out with metal catalysts quite often. Among these catalysts lanthanide metal catalysts have received most interest as they have well-defined structures and can be used as single-component catalysts. A number of lanthanide metal (III) based catalysts including lanthanocene hydride,¹⁴ lanthanide alkoxides (phenoxides),^{15–21} and triamidinates and triguanidinates^{22–24} have been found to be the efficient catalysts. Lanthanide metal (II) complexes have been reported to be highly active catalysts for the ring-opening polymerization of ϵ -caprolactone,²⁵ while the utility of lanthanide metal

(II) complexes as the catalysts for the polymerization of cyclocarbonate has been quite limited. Evans and Katsumata²⁶ reported several lanthanide (II) complexes, including (C₅Me₅)₂Sm(THF)₂, (C₉H₇)₂Sm(THF)_{1.5}, (C₁₃H₉)₂Sm(THF)₂, [(Me₃Si)₂N]₂Sm(THF)₂, and SmI₂(THF)₂ to be the active catalysts for the copolymerization of ethylene carbonate and ϵ -caprolactone. Yasuda et al.^{11–13} addressed the homopolymerization and copolymerization of MTC by (C₅Me₅)₂Sm(THF)₂.

As part of our recent studies on the chemistry of lanthanide (II) aryloxy complexes,^{27–29} we have investigated their catalytic activity for the ring-opening polymerization of TMC and the copolymerization of TMC and ϵ -CL. In this article, we describe the results on the ring-opening polymerization of TMC, and the random copolymerization of TMC and ϵ -CL using (ArO)₂Ln(THF)₃ (Ln = Sm **1**, Yb **2**; ArO = 2,6-di-*tert*-butyl-C₆H₃O) as catalysts, as well as the structure and thermal behavior of the copolymers P(TMC-*co*-CL) by ¹H NMR, ¹³C NMR, GPC, and DSC analysis.

EXPERIMENTAL

Materials

TMC was prepared by the exchange reaction of 1,3-propanediol and diethyl carbonate, recrystallized and dried before use.³⁰ ϵ -CL was purchased from Acros, dried over CaH₂ and distilled under Ar atmosphere

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TABLE I
Ring-Opening Polymerization of TMC Catalyzed by $(\text{ArO})_2\text{Ln}(\text{THF})_3^a$

Entry	Initiator	[M]/[I] ^b	Temperature (°C)	Yield ^c (%)	M_n (10^4)	M_w/M_n ^d
1	$(\text{ArO})_2\text{Sm}(\text{THF})_3$	100	40	86	2.03	2.07
2	$(\text{ArO})_2\text{Sm}(\text{THF})_3$	500	40	65	4.55	2.51
3	$(\text{ArO})_2\text{Yb}(\text{THF})_3$	100	25	58	2.99	1.82
4	$(\text{ArO})_2\text{Yb}(\text{THF})_3$	100	40	77	1.69	2.08
5	$(\text{ArO})_2\text{Yb}(\text{THF})_3$	100	60	79	2.69	1.97
6	$(\text{ArO})_2\text{Yb}(\text{THF})_3$	100	80	81	2.20	2.11
7	$(\text{ArO})_2\text{Yb}(\text{THF})_3$	200	25	54	3.48	2.07
8	$(\text{ArO})_2\text{Yb}(\text{THF})_3$	200	40	70	3.75	2.12

^a Conditions: $[\text{TMC}] = 1 \text{ mol L}^{-1}$, Time = 30 min, toluene.

^b $[\text{M}]$ = monomer concentration; $[\text{I}]$ = initiator concentration.

^c Yield = weight of the obtained polymer/weight of the used monomer.

^d Measured by GPC calibrated with standard polystyrene samples.

at reduced pressure. Lanthanide (II) aryloxide complexes $(\text{ArO})_2\text{Ln}(\text{THF})_3$ ($\text{Ln} = \text{Sm}$ **1**, Yb **2**) were synthesized and purified according to the literature procedures.²⁷ All solvents were analytical grade and were distilled from Na/benzophenone ketyl prior to use.

Polymerization of TMC

All polymerizations were carried out under dry argon atmosphere with a similar procedure. A typical polymerization reaction is given below: a 50-mL Schlenk flask equipped with a magnetic stir bar was charged with a solution of TMC (0.306 g, 3 mmol) in toluene (2.40 mL), which was kept at 40°C. A toluene solution of catalyst **1** ($5.0 \times 10^{-2} \text{ mol L}^{-1}$, $3 \times 10^{-2} \text{ mmol}$) was added to this solution using a rubber septum and syringe. The mixture was vigorously stirred for a certain time, quenched by methanol with 2% HCl, and the polymers precipitated from methanol. The polymers PTMC were washed with methanol, filtered, and dried under vacuum to constant weight. The polymer yield was determined gravimetrically.

Copolymerization of TMC and ϵ -CL

All copolymerizations were carried out in a 50-mL Schlenk flask under dry argon atmosphere. For a typical procedure, TMC (0.26 g, 2.52 mmol), ϵ -CL (0.28 mL, 2.52 mmol), and toluene (4.04 mL) were added into a dry flask at 40°C in turn. Then the toluene solution of catalyst **1** ($5.0 \times 10^{-2} \text{ mol L}^{-1}$, $5.04 \times 10^{-2} \text{ mmol}$) was introduced by syringe into the reaction solution. The contents of the flask were then vigorously stirred for 10 min at 40°C. The copolymerization was quenched by adding a 2% solution of HCl in methanol. The polymer precipitated from methanol and was dried under vacuum to constant weight. The copolymer yield was determined by gravimetry.

Oligomers for end group analysis

The oligomerization of TMC was carried out with catalyst **1** in toluene at room temperature under the condition of $[\text{TMC}]/[\text{1}]$ (molar ratio) of 10. The reaction was terminated by adding 1 mL of 2% HCl/MeOH after 3 h. The oligomer was precipitated from methanol. The product was dissolved in THF, followed by precipitation in methanol. After filtration, the white product was dried *in vacuo*.

Measurements

Gel-permeation chromatography (GPC) measurements calibrated to commercial polystyrene standards were performed on a PE PL-GPC50 apparatus with two PLgel 10 μm MIXED-B columns in THF (1.0 mL/min) at 40°C. ¹H NMR and ¹³C NMR spectra were recorded on a Unity Inova-400 spectrometer

TABLE II
Homopolymerization of TMC Catalyzed by **1**^a

Entry	[M]/[I] ^b	Time (min)	Yield ^c (%)	M_n (10^4)		M_w/M_n ^e
				Calcd ^d	Obsd ^e	
1	100	30	86	0.88	2.03	2.07
2	200	30	76	1.55	2.94	2.16
3	500	30	65	3.32	4.55	2.51
4	1000	30	10	1.02	2.87	2.21
5	200	2	56	1.14	2.26	2.06
6	200	5	66	1.35	3.61	1.94
7	200	10	70	1.43	3.37	2.04
8	200	60	83	1.69	2.94	1.95
9	200	90	86	1.75	2.88	2.35

^a Conditions: $[\text{TMC}] = 1 \text{ mol L}^{-1}$, 40°C, toluene.

^b $[\text{M}]$ = monomer concentration; $[\text{I}]$ = initiator concentration.

^c Yield = weight of the obtained polymer/weight of the used monomer.

^d M_n (calcd) = (M_w of TMC) \times $[\text{M}]/[\text{I}] \times$ (polymer yield).

^e Measured by GPC calibrated with standard polystyrene samples.

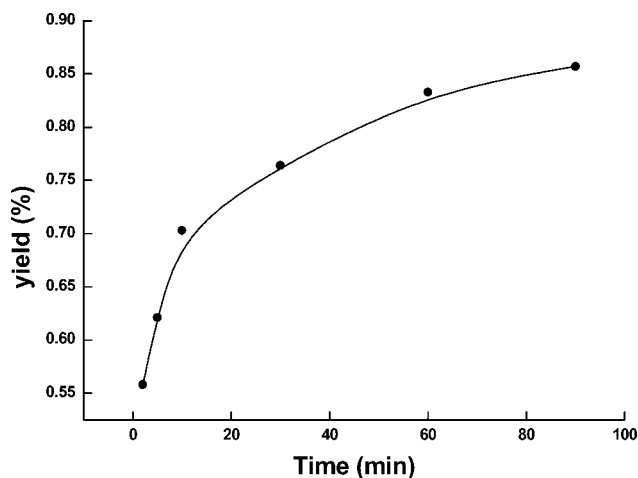


Figure 1 The curve of yield vs. polymerization time with **1** as the initiator. Conditions: $[TMC]/[1] = 200$, $[TMC] = 1 \text{ mol L}^{-1}$, 40°C , toluene.

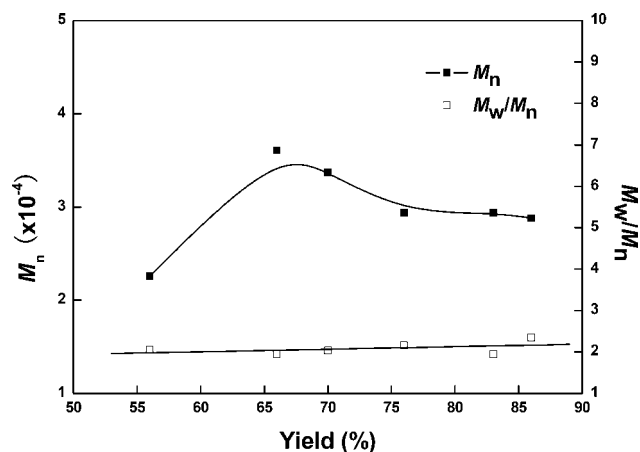


Figure 2 Yield vs. M_n and M_w/M_n plots. Conditions are the same as Figure 1.

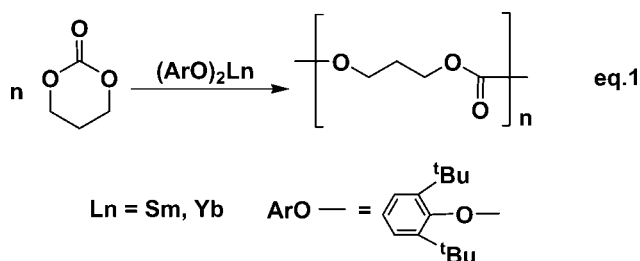
in CDCl_3 and C_6D_6 at 400 and 100 MHz with tetramethylsilane as internal standards, respectively. The copolymer composition was calculated comparing the area of the PCL signal (at 2.3 ppm) and PTMC one (at 2.05 ppm). Differential scanning calorimetric (DSC) curves were taken on a Perkin-Elmer DSC-7 apparatus. Cyclohexane and pure water were used as standards for temperature calibration. To eliminate the heat history, each sample was heated fast from room temperature to $+120^\circ\text{C}$ then cooled to -60°C and heated to $+120^\circ\text{C}$ for recording with a heating rate of $10^\circ\text{C}/\text{min}$. The glass transition temperature (T_g) was taken as the midpoint of the heat capacity change and the peak melting temperature (T_m) was determined from the melting endotherm, respectively.

RESULTS AND DISCUSSION

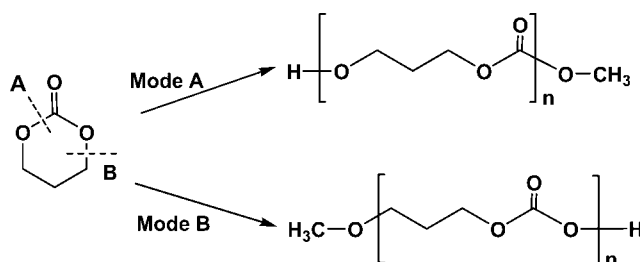
Homopolymerization of TMC

The homopolymerization of TMC was first tried by use of lanthanide metals (II) 2,6-di-*tert*-butylphenoxide complexes $(\text{ArO})_2\text{Ln}(\text{THF})_3$ ($\text{Ln} = \text{Sm}$ **1**, Yb **2**) as single-component catalysts as shown in Eq. (1). The polymerizations went smoothly under various conditions and the results are presented in Table I. Both complexes exhibited moderate reactivity. The dependence of polymerization activity on the metal was observed, with the sequence of $\text{Yb}(\text{II}) < \text{Sm}(\text{II})$. For example, the polymer yield reached to 86% at 40°C for 30 min at the molar ratio of 100 ($[\text{M}]/[\text{I}]$) by using complex **1** (Table I entry 1), while 77% for complex **2** (Table I entry 4). Even the molar ratio of $[\text{M}]/[\text{I}]$ increased to 500, the polymer yield of 65% could be gained for catalyst **1** (Table I entry 2). Such

a sequence of $\text{Yb}(\text{II}) < \text{Sm}(\text{II})$ in reactivity was often observed in the homogeneous catalyses catalyzed by lanthanide metal (II) complexes²⁷⁻²⁹ and may be contributed to the lower oxidation potentials of Sm in comparison with Yb.



The conversion increased with an increasing of temperature from 25 to 80°C in both cases of $[\text{M}]/[\text{I}] = 100$ and 200 for **2** as the initiator. However, the molecular weights and molecular weight distributions of the resulting polymers were almost unchanged (Table I entries 3–8). The increase in the initiator concentration led to the increase in polymer yield, the decrease of M_n of the resulting polymer, while the polydispersity of PTMC remained rela-



Scheme 1 Ring-opening modes of TMC: mode A for acyl-oxygen bond cleavage and mode B for alkyl-oxygen bond cleavage.

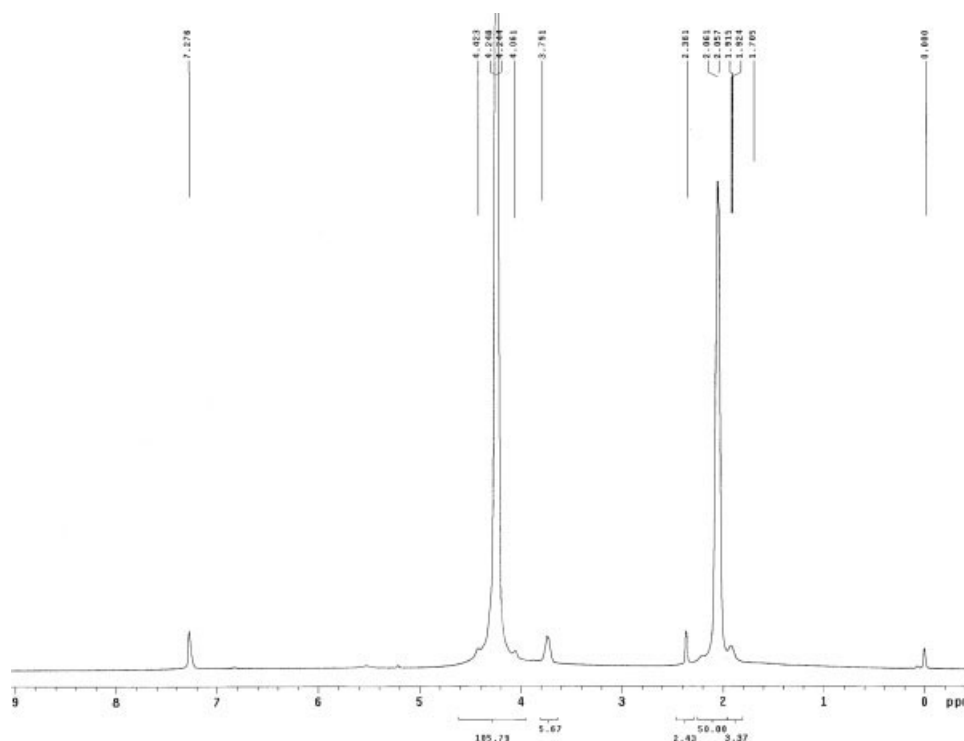


Figure 3 ^1H NMR spectrum of oligomer of TMC catalyzed by **1** with a molar ratio of $[\text{TMC}]/[\mathbf{1}] = 10$.

tively broad and kept almost unchanged (Table II entry 1–4).

The reactivity observed here is comparable with those of divalent lanthanocene complex $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$,^{11–13} and trivalent complex $\text{Sc}(\text{OAr}')_3$ ($\text{Ar}'\text{O} = 2,6\text{-di-}t\text{-butyl-4-MeC}_6\text{H}_2\text{O}$),¹⁷ but lower than those of LnCl_3 ¹⁶ and $\text{La}(\text{OAr}')_3$.²¹ In comparison with the above catalysts, the present lanthanide (II) aryloxide complexes gave the polymers with relatively broader molecular-weight distributions ranged from 1.82 to 2.51.

TABLE III
TMC and $\epsilon\text{-CL}$ Copolymerization Catalyzed by **1**^a

Entry	Feeding Molar Ratio (TMC: $\epsilon\text{-CL}$)	Yield ^b (%)	M_n^c (10^4)	M_w/M_n^c	TMC: $\epsilon\text{-CL}$ in polymer ^d
1	100 : 0	77	1.48	2.06	–
2	80 : 20	55	1.72	2.01	78 : 22
3	60 : 40	75	1.68	1.94	57 : 43
4	50 : 50	85	2.37	1.94	44 : 56
5	40 : 60	80	2.30	1.87	35 : 65
6	20 : 80	78	2.86	1.73	16 : 84
7	0 : 100	100	3.78	1.71	–

^a Conditions: $[\text{TMC} + \epsilon\text{-CL}] = 1.0 \text{ mol L}^{-1}$, $[\text{TMC} + \epsilon\text{-CL}]/[\mathbf{1}] = 100$, 10 min, 40°C , toluene.

^b Yield = weight of the obtained polymer/weight of the used monomer.

^c Measured by GPC calibrated with standard polystyrene samples.

^d Calculated from ^1H NMR spectrum, molar ratio.

Figures 1 and 2 depict the dependences of yields on polymerization time, and molecular weights and molecular weight distributions of the polymers on yields, respectively. The yield increased with the polymerization time. The molecular weight first

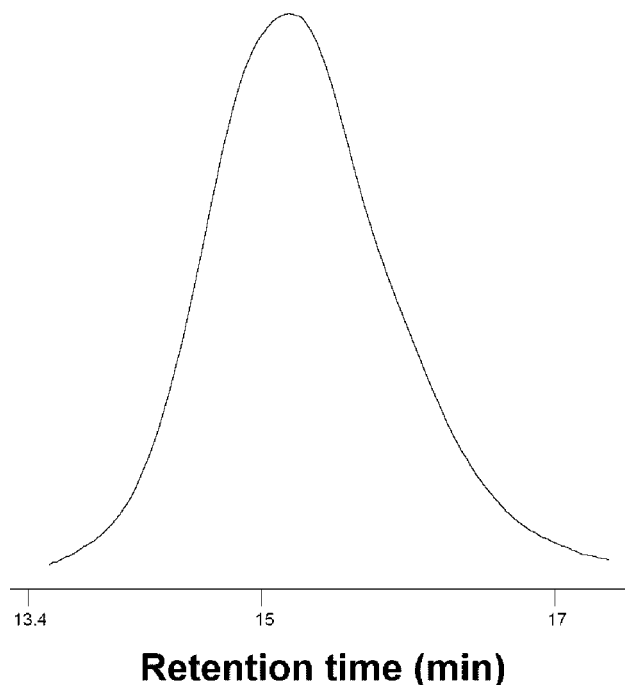


Figure 4 GPC curve of $\text{P}(\text{TMC-co-CL})$ catalyzed by **1** (entry 4 in Table III).

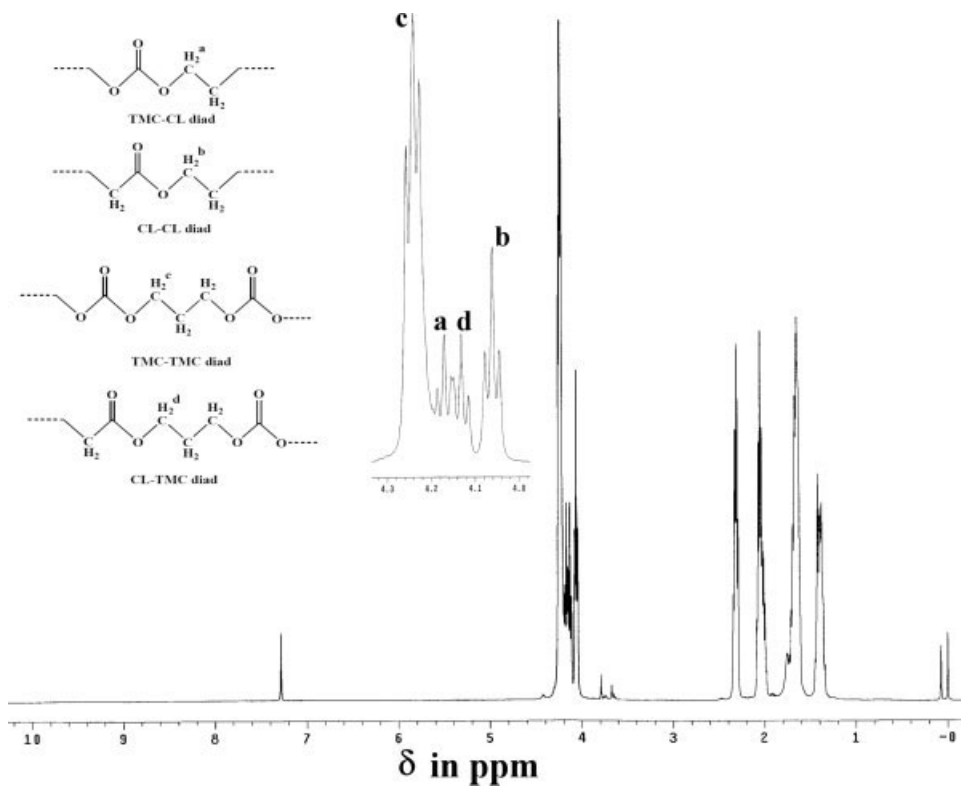


Figure 5 ^1H NMR spectrum of the random copolymer of TMC with CL (entry 3 in Table III).

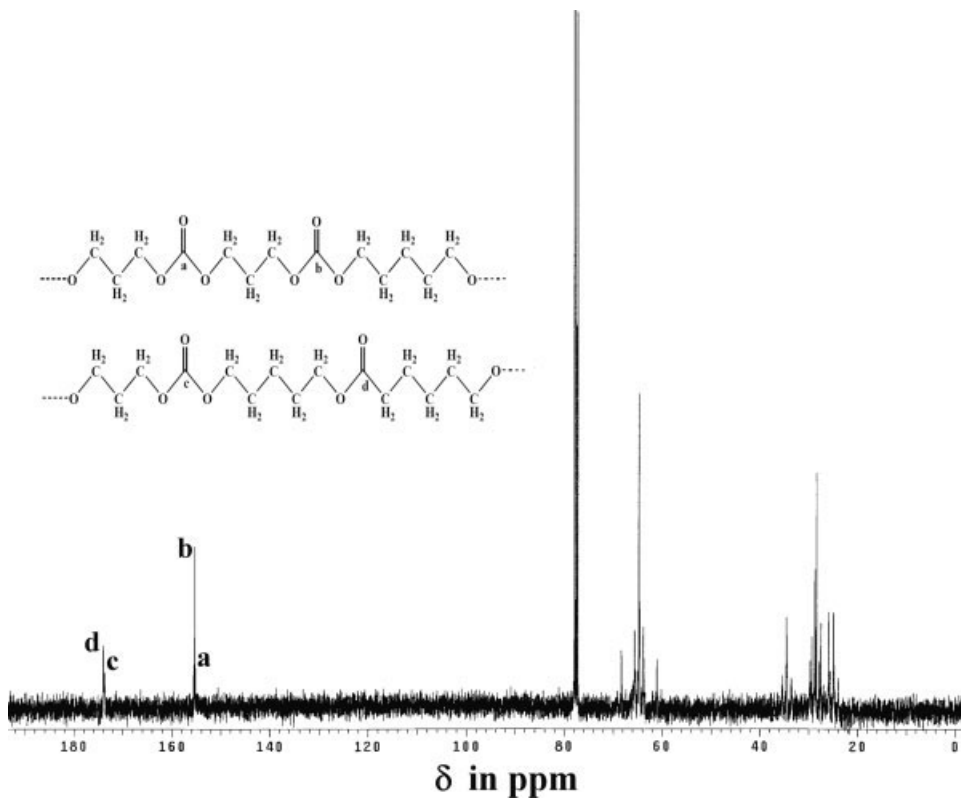


Figure 6 ^{13}C NMR spectrum of the random copolymer of TMC with CL (entry 3 in Table III).

TABLE IV
Phase Transition Values of Homopolymers and Copolymers of TMC and ϵ -CL

Entry	Polymer	M_n (10^4)	T_g ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	ΔH (J/g)	Composition (mol%) (TMC: ϵ -CL)
1	PTMC	1.48	-17.1	42.2	25.22	100 : 0
2	P(TMC- <i>co</i> -CL)	1.72	-37.2, -26.5	39.9	1.17	78 : 22
3	P(TMC- <i>co</i> -CL)	1.68	-48.5, -30.6	36.8	8.26	57 : 43
4	P(TMC- <i>co</i> -CL)	2.37	-45.1	43.7, 54.7	22.58	44 : 56
5	P(TMC- <i>co</i> -CL)	2.30	-51.1	38.0, 50.6	34.07	35 : 65
6	P(TMC- <i>co</i> -CL)	2.86	-	42.8, 62.3	71.6	16 : 84
7	PCL	3.78	-	64.4	97.1	0 : 100

increased, pass the highest value, decreased with the conversion, while the molecular weight distribution became gradually broader. The gradually widened molecular weight distribution indicated that transesterification reaction may be accompanied with the ring-opening polymerization.

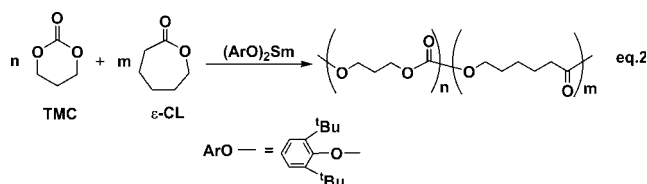
Homopolymerization mechanism aspects

It has been reported the ring-opening polymerization of cyclocarbonate by lanthanide metal (III) catalysts takes place according to a coordination-insertion mechanism, and can proceed by either acyl-oxygen bond cleavage or alkyl-oxygen bond cleavage as illustrated in Scheme 1.¹⁷ To clarify the reaction mechanism, a sample of low molecular weight PTMC terminated by CH_3OH was prepared and subjected to ^1H NMR analysis as shown in Figure 3. The singlet peak at 3.73 ppm assigned to the esterified methyl group of one end of PTMC chain and no signal at 3.0–3.5 ppm, which would be assigned to methyl ether end group was detected in the spectrum. Therefore, it could be concluded that the ring-opening polymerization of TMC undergoes an acyl-oxygen bond cleavage (Mode A in Scheme 1). It was observed that the color of the initiators solution turned from brown for **1** and orange for **2** to yellow as soon as the initiators were injected into the systems. The color change indicated that the central metals Sm (II) and Yb (II) were oxidized to Sm (III) and Yb (III), respectively. This means the real active species for the polymerization of TMC should be a trivalent Sm (III) and Yb (III) aryloxide derivatives. The detailed study of the active species is proceeding in our laboratory.

Copolymerization of TMC and ϵ -CL with **1**

The copolymerization is a direct access to provide the copolymer with the properties required for the different applications by changing the composition of the copolymer. Adding monomers simultaneously is a widely used method for the synthesis of random copolymers. Thus, copolymerization of TMC and ϵ -

CL was first carried out by $(\text{ArO})_2\text{Sm}(\text{THF})_3$ as shown in Eq. (2) and the results were summarized in Table III. It can be seen from Table III that complex **1** can efficiently initiate the copolymerization of TMC and ϵ -CL as single-component catalyst at 40°C . The copolymer was obtained in 85% yield after 10 min, when the feeding molar ratio of the monomers is 50 : 50 under the conditions shown in Table III. All the copolymers obtained here have a unimodal molecular weight distribution indicating the polymers obtained are pure copolymers without both homopolymers of ϵ -caprolactone and TMC. A GPC curve for the copolymer obtained at the molar ratio of monomers of 50:50 is shown in Figure 4 as an example.



The ^1H and ^{13}C NMR spectra of this copolymer with the assignments of characteristic signals detected are shown in Figures 5 and 6, respectively, by which the molar ratio of TMC units and ϵ -CL units in the copolymer is calculated to be 57 : 43. The four kinds of peaks at δ 4.0–4.3 ppm indicate the hydrogen atoms of OCH_2 having four chemical surroundings as shown in Figure 5. High intensities of H^a and H^d provide an evidence for the direct bonding of CL with TMC. Calculated from the intensities of H^a , H^b , H^c , and H^d in the ^1H NMR spectrum, the percentages of diad structures of CL-CL, TMC-TMC, and TMC-CL, CL-TMC are 27.0%, 40.9%, and 32.1%, respectively.¹⁷ The four groups of peaks at 155.3–174.0 ppm shown in Figure 6, indicate four kinds of carbonyl groups. According to previously published values,^{31–34} C^b and C^c attribute to the carbonyl atoms in the CL-TMC and TMC-CL units, respectively, and the presence of signals at 68.2 and 61.0 ppm is the

characteristic of random copolymers. Therefore, both the ^1H and ^{13}C NMR spectra confirm the product to be a random copolymer rather than the blend.

DSC is another good method to confirm the random structure of the copolymers. It is well known that T_m of PCL shifts in the range 50–66°C depending on its molecular weight and crystallinity.¹⁷ All the results for DSC determination are summarized in Table IV. In our case, a T_m of 64.4°C for homopolymer PCL and a T_g of -17.1°C and a T_m of 42.2°C for homopolymer PTMC are detected (Table IV entries 7 and 1). In DSC spectra of the P(TMC-co-CL) new T_m peaks appeared, while the T_m peaks for homoPCL and homoPTMC disappeared, thus corroborating the random structure of the copolymers. However, all the DSC spectra of copolymers show two separate T_g or T_m peaks, which are dependent on the composition. The results indicate the presence of blocky structures of PCL and PTMC in the copolymer chains.^{6,16,17,35} Thereby, copolymers having different monomer compositions show quite distinct thermal behavior.

CONCLUSIONS

Lanthanide (II) 2,6-di-*tert*-butylphenoxide complexes (ArO)₂Ln(THF)₃ (Ln = Sm **1**, Yb **2**) are developed to catalyze ring-opening homopolymerization of TMC and random copolymerization of TMC and ϵ -CL as single component initiators for the first time. The results showed that the reactivity depends on the central metal with the sequence of Yb(II) < Sm(II). The P(TMC-co-CL) obtained were fully characterized by ^1H NMR, ^{13}C NMR, GPC, and DSC analysis to be random copolymer. Copolymers having different monomer compositions show quite distinct thermal behavior.

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